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Formation and Migration of NCO Species on Ag/SiO_2 Catalyst

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Abstract The adsorption of HNCO has been investigated on Ag/SiO_2 catalyst by means of FTIR spectroscopy. Adsorption of HNCO on the reduced sample at 190 K produced an absorption band at 2,170 cm^{-1} attributed to NCO bonded to Ag. Annealing the adsorbed layer under continuous degassing, the 2,170 cm^{-1} band gradually attenuated and at the same time a spectral feature at 2,300 cm^{-1} due to Si–NCO developed. From these spectral changes it was inferred that NCO bonded to Ag spilt over onto silica.

Keywords Ag/SiO_2 catalyst · Reduction of NO with ethanol · HNCO adsorption · Formation of Ag–NCO · Spillover of NCO

1 Introduction

Since seventies an extensive research has been devoted to the catalytic reaction between NO and CO pollutants on supported metals [1, 2]. One of the interesting features of this process is the formation of NCO surface complex detected by IR spectroscopy [3–9]. From the subsequent extensive studies the following main features were established: (i) the asymmetric stretch of NCO sensitively depends on the nature of the support—the highest frequency, 2,300 cm^{-1}, was registered for silica-supported, and the lowest one, at 2,210 cm^{-1}, for titania-supported Pt metals [10, 11]: (ii) the amount of NCO exceeds by more than 1 order of magnitude the number of surface Pt atoms [12]. Note that no NCO species was detected on metal free supports like alumina, silica, magnesia, ceria and titania under similar experimental conditions [3–12]. On the basis of these findings it was inferred NCO species is formed on the metals, but after its production it spills over onto the oxidic support, when it is stabilized [8, 9, 10]. Adsorption of HNCO on metal-free oxide-supports produced the same absorption bands as observed in the NO + CO reaction confirming this conclusion [11, 13, 14]. In the further evaluation of the chemistry of NCO species, the use of HNCO and studies performed metal single crystals in UHV system greatly contributed [15–27]. It appeared that the asymmetric stretch of NCO on metals is between 2,170–2,190 cm^{-1}, and the NCO bonded to the metals decomposes at 300–423 K. Although the role of isocyanate species in the NO + CO reaction is still debated, it was clearly demonstrated quite early that NCO reacts with water resulting in the undesired formation of ammonia [12]. Following the pioneer works, NCO surface species has been identified on different kinds of catalysts in the reduction of NO with various carbon-containing compounds [28]. The positions of NCO bands on various solids and the chemistry of NCO species showed a good agreement with those established before.

The increased use of oxygenated organic compounds, particularly ethanol, as fuel or additives for automotive vehicles required the study of the reaction between NO and ethanol. It was found that ethanol is extremely effective for NO_x reduction over Ag/Al_2O_3, which displays high tolerances to water and SO_2 [29–36]. FTIR spectroscopy revealed the formation of two absorption bands at

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2,228–2,235 and 2,255–2,260 cm^{-1}, which were attributed to NCO surface species. As regards the location of NCO different views were expressed. The first band was attributed to the vibration of Ag–NCO, whereas the second one to that of Al–NCO [29, 32]. Alternatively both bands were ordered to Al–NCO [34, 35]. In the explanation of the occurrence of NCO on alumina, the migration of nitrogen, carbon and CN species from Ag onto alumina, and the subsequent formation of NCO was assumed [29–36].

The primary aim of the present study is as follows: (i) to produce NCO species bonded to the Ag, and to determine unambiguously the vibration characteristics of Ag–NCO, and (ii) to ascertain the migration of NCO from the Ag onto supports. Method applied is FTIR spectroscopy. For this purpose we choose silica support, which has some advantages compared to other ones: (i) the migration of NCO from metal to silica is slow, and (ii) the dissociation of HNCO on silica is restricted at lower temperature. This makes possible to determine the IR characteristic of NCO *bonded* to *metal*, and to follow the diffusion of NCO from metal onto silica.

2 Experimental

Ag/SiO_2 samples were prepared by impregnation of silica (Cab–O–Sil), 200 m^2/g in the solution of $AgNO_3$. The dried suspension was pressed into self-supporting wafers (30 × 10 mm ~10 mg/cm^2) calcined in the IR cell at 573 K for 60 min and oxidized at 873 K for 60 min. In certain cases the calcined sample was reduced at 673 K in the presence of 100 Torr H_2 for 60 min. HNCO was prepared by the dropwise addition of a saturated aqueous solution of potassium cyanate (KOCN, BDH Chemicals, 98% purity) to concentrated phosphoric acid (Baker, 85% by weight in water) under vacuum [13]. The HNCO vapor produced in this reaction was condensed at 190 K cooled by a dry ice/acetone bath under dynamic vacuum conditions. This product was twice statically vacuum distilled from 240 to 190 K to remove mostly CO_2, NH_3, and H_2O impurities. The purity of HNCO has been checked by MS: water was not detected. The HNCO was stored at LN_2 temperature. A mobile IR cell housed in a metal chamber was used. The sample can be heated and cooled to 150–200 K in situ. The IR cell can be evacuated to 10^{-5} Torr using a turbo molecular pumping system. Infrared spectra were recorded with a Biorad (Digilab. Div. FTS 155) instrument with a wavenumber accuracy of ±4 cm^{-1}. All the spectra presented in this study are difference spectra.

3 Results and Discussion

In order to determine the absorption band of NCO bonded to Ag, HNCO was adsorbed on 2% Ag/SiO_2 at 190 K. Experiments have been performed on reduced and oxidized samples. Spectra for reduced catalyst are displayed in Fig. 1A. At very low HNCO pressure we obtained a weak signal at ~2,170 cm^{-1} in the frequency region of asymmetric stretch of NCO. On increase of the HNCO pressure the 2,170 cm^{-1} peak intensified and a high frequency band at 2,262 cm^{-1} appeared. This band is no doubt is due to the weakly and molecularly adsorbed HNCO, which was eliminated during degassing at ~260 K. In order to assist the assignment of absorption bands formed, we collected the positions of asymmetric stretch of NCO species bonded to various metals and oxides in the Table 1. On the basis of these data, the 2170 cm^{-1} band is assigned to the vibration of NCO attached to Ag.

Further annealing the adsorbed layer during continuous degassing first led to the gradual attenation of the 2,170 cm^{-1} peak. This spectral feature disappeared completely above 573 K. At the same time the weak band at 2,302 cm^{-1} detected first by 260 K gradually gained

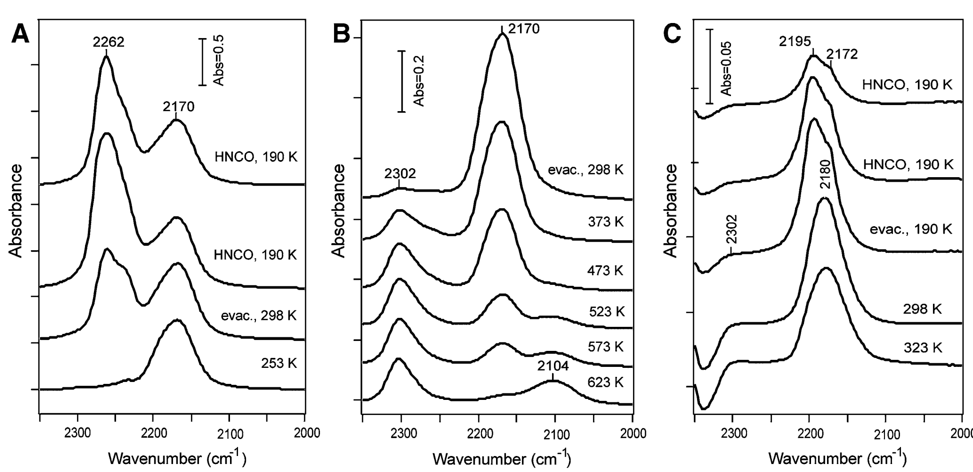

Fig. 1 FTIR spectra of 2% Ag/SiO_2 following HNCO adsorption 8.0–9.5 × 10^{-3} mbar at 190 K and after subsequent heating under continuous evacuation. Reduced sample (**A**, **B**), oxidized sample (**C**). In the case of (**C**) we used only 6.2–9.8 × 10^{-4} mbar of HNCO

Table 1 The position of asymmetric stretching frequency of the adsorbed NCO formed in the dissociative adsorption of HNCO

	cm^{-1}	Refs.
TiO_2	2,187, 2,210	11, 37
CeO_2	2,180, 2,210	14
Cr_2O_3	2,212	11, 37
MgO	2,223	11, 37
Al_2O_3	2,260	11, 37
SiO_2	2,300–2,310	11, 37
ZSM-5	2,260, 2,300	11, 37
Pt metals (single crystals)	2,170–2,190	15–25
Cu (111) (100)	2,201	18
Au (on SiO_2)	2,190	14
Ag (on SiO_2)	2,170	Present study

intensity at the expense of absorption feature at 2,170 cm^{-1}. The 2302 cm^{-1} band dominated the spectrum above 473 K (Fig. 1B). Taking into account the results of previous studies (Table 1), the 2,302 cm^{-1} band is attributed to the asymmetric stretch of NCO bonded to Si.

Repeating this experimental series with oxidized Ag/SiO_2 we found somewhat different picture. Exposing the 2% Ag/SiO_2 to a very small amount of HNCO (6.2–9.8 $\times$ 10^{-4} mbar) produced two absorption bands at 2,172 and 2,195 cm^{-1} in the region of 2,100–2,200 cm^{-1} (Fig 1C). Annealing the sample resulted in a broad band peaking at 2,180 cm^{-1}. The development of the Si–NCO group already occurred around 190 K. Previous works revealed that the presence of adsorbed oxygen stabilizes the NCO species on metal, and shifts the asymmetric stretch to higher wavenumbers [18, 20, 23, 27]. Accordingly, we propose that the new feature at 2,195 cm^{-1} is due to Ag–NCO perturbed by coadsorbed oxygen.

Spectra obtained on pure SiO_2 under similar experimental conditions are presented in Fig. 2A. At the temperature of the adsorption of HNCO, at ~190 K, we observe only the characteristic band due to molecularly adsorbed HNCO, which disappeared around 298 K under continuous degassing. There was no sign of the absorption feature at 2,302 cm^{-1} at any temperature in the range of 260–673 K (Fig. 2A). However, this band developed in the FTIR spectrum of SiO_2, when the sample was heated in the presence of gaseous HNCO above 300 K, suggesting that the dissociation of HNCO on SiO_2 is an activated process. The fact that the 2,302 cm^{-1} band appeared in the presence of Ag at much lower temperatures and even in the absence of HNCO suggests that HNCO underwent dissociation over silver

$$\mathrm{HNCO} + 2\mathrm{Ag} = \mathrm{Ag} - \mathrm{NCO} + \mathrm{Ag} - \mathrm{H}$$

and the NCO spillt over from Ag onto SiO_2 to give Si–NCO surface species, similarly as in the case of silica-supported Pt metals [11–14, 37–40]. We assume that we can count on the occurrence of similar processes in the catalytic reaction of the C_2H_5OH + NO + O_2 gas mixture.

4 Conclusions

(i) Adsorption of HNCO underwent dissociation over Ag/SiO_2 above 190 K producing an absorption band at 2,170 cm^{-1} attributed to Ag–NCO;

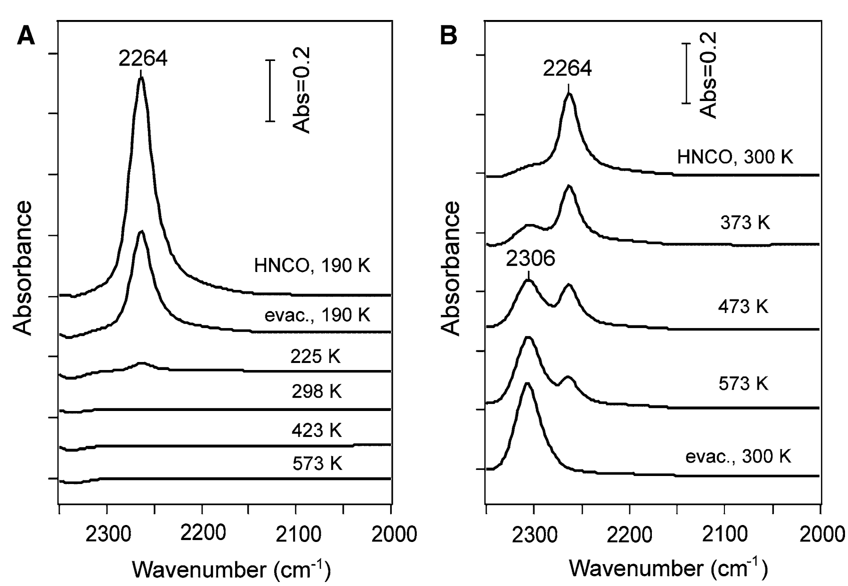

Fig. 2 FTIR spectra of SiO_2 following HNCO adsorption at 190 K and after subsequent heating under continuous evacuation (**A**), and after heating in the presence of 2.5 $\times$ 10^{-1} mbar of HNCO (**B**)

(ii) NCO species on Ag was found to be much more stable than on Pt metals;

(iii) At higher temperature the NCO species migrated from the Ag onto SiO_2 resulting in the appearance of a stable band at 2,300 cm^{-1} due to Si–NCO.

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